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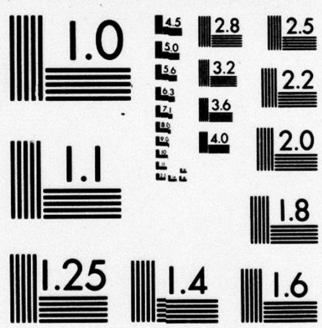

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Electronic Structure of and Bonding in Antimony Phthalocyanine Complex

by

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The electronic and bonding structures of antimony phthalocyanine complex has been investigated by X-ray photoelectron spectroscopy and resonance Raman spectroscopy. Although the elemental analysis accords with the structure of Pc:Sb.Sb:Sb.Sb:Pc previously reported by Barret et al., our spectroscopic studies rule out the structure. We now propose a tentative structure of antimony phthalocyanine complex such as Pc(Sb(II)O)$_2$ or [-Pc-Sb(III)$\genfrac{}{}{0pt}{}{O}{O}$Sb(III)-]-$_n$ based on the photoelectron spectra of Sb_{3d} and N_{1s} regions

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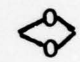
and resonance Raman data.

ABSTRACT

The electronic and bonding structures of antimony phthalocyanine complex has been investigated by X-ray photoelectron spectroscopy and resonance Raman spectroscopy. Although the elemental analysis accords with the structure of Pc:Sb·Sb:Sb·Sb:Pc previously reported by Barret et al., our spectroscopic studies rule out the structure. We now propose a tentative structure of antimony phthalocyanine complex such as Pc(Sb(II)O)$_2$ or [-Pc-Sb(III)  -Sb(III)-]-$_n$ based on the photoelectron spectra of Sb_{3d} and N_{1s} regions and resonance Raman data.

ELECTRONIC STRUCTURE OF AND BONDING

IN ANTIMONY PHTHALOCYANINE COMPLEX

INTRODUCTION

Continuing our studies of metal containing phthalocyanine complexes [1] as a part of macrocyclic (N_4) chemistry [2], we investigated electronic and bonding structures of antimony phthalocyanine complex by X-ray photoelectron spectroscopy (ESCA) and resonance Raman spectroscopy. A reaction between antimony and phthalonitrile was first reported by Byrne, Linstead, and Lowe [3] in 1934, and antimony phthalocyanine was isolated as a formula, $PcSb_2$ [4]. A proposed structure of the compound is Pc:Sb·Sb:Sb·Sb:Pc, where the two terminal antimony atoms are located in the center of phthalocyanine rings and are joined by a chain of two antimony atoms. Up to now, however, no further effort has been exerted to elucidate the bonding structure of antimony phthalocyanine complex. The complex is much less stable than most members of phthalocyanine compounds. When crystallized from chloronaphthalene [4] and THF, it was decomposed yielding metal-free compounds. Due to the lack of a suitable solvent, neither UV nor visible spectroscopy is effective for characterization of antimony phthalocyanine.

X-ray photoelectron spectroscopy, on the other hand, proved to be a useful tool for the structural study of phthalocyanine compounds. Two types of nitrogens were found by ESCA in metal-free phthalocyanine, the aza type and pyrrole type nitrogens, where the N_{1s} binding energy of the former is c.a. 1.5eV lower than that of the latter [5]. On metal complexation, in contrast, the eight nitrogens give a single sharp N_{1s} peak which indicates a small energy separation between four equivalent central nitrogens and four meso-bridging nitrogens [1a), 5].

It is also well known that measurements of core binding energies provide good information to elucidate oxidation states of metals in complexes. Along this line,we measured N_{Is} and Sb_{3d} photoelectron spectra of antimony phthalocyanine complex together with resonance Raman spectra in the range 200cm^{-1} $\sim$1800 cm^{-1} in order to elucidate bonding structure of the complex.

EXPERIMENTAL

Antimony phthalocyanine was synthesized and purified by literature methods [4]. Powdered antimony was obtained from Fischer Science Co. and was used without any further purification. Elemental analysis on the product was performed by Schwarzkopf Microanalytical Laboratory, New York. Anal. calcd for $PcSb_2O_2$: C, 48.77; N, 14.22; H, 2.05; Sb, 30.91; for $PcSb_2$: C, 50.70; N, 14.78, H, 2.13; Sb, 32.13. Found: C, 50.30; N, 13.95; H, 2.58; Sb, 31.62. On crystalization form THF, the compound yielded metal-free product(s). Anal. Found: N, 10.56; Sb < 1.00.

Diantimony phthalocyanine $PcSb_2$ is commercially available (Eastman Kodak Co.) in a practical purity. However, the result of elemental analysis on the sample is far from the calculated values for $PcSb_2$. Found: N, 14.91; Sb, 22.46. Then, the Eastman's sample was washed by methanole for 2 days at 63°C. Found: N, 18.19; Sb, 10.47. These values again much deviate from "$PcSb_2$", and are even close to "$[Pc_2Sb]H$" or "$[Pc_2Sb]H \cdot 2CH_3OH$" : the former requires N, 19.52; Sb, 10.61 while the latter requires N, 18.49; Sb, 10.05. Further discussion, however, will not be made in this report.

X-ray photoelectron spectra were measured by a Hewlett-Packard 5950Å ESCA spectrometer using Al X-ray anode. The typical residual pressures in this system were in the 10^{-9} torr range. The charging effects were neutralized by using an electron flood gun. The sample (antimony phthalocyanine) was prepared by mounting on double stick scotch tape. Raman spectra were recorded on a Varian Cary Model 82 laser Raman spectrometer with a Coherent Radiation Model 53 argon ion laser.

RESULTS AND DISCUSSION

Although the elemental analysis of the product, antimony phthalocyanine, seems to fit for the formula $PcSb_2$, it is difficult to figure out the possible structure for the forumula by ordinary valency requirement of antimony. Crystalization from THF gave rise to a decomposition of the compound and UV and visible spectroscopy were not effective for the structural study. ~~We then used~~ the X-ray electron spectroscopy and Raman spectroscopy WAS THEN USED in order to elucidate the structure.

The X-ray photoelectron spectra of Sb_{3d} and N_{1s} regions are given in Figures 1 and 2, respectively. The binding energies were calibrated to the intense C_{1s} photopeak observed in the lowest energy side. The peak has been assigned to the carbon atoms of having aromatic hydrocarbon character in the phthalocyanine ring. The binding energy of the standard peak is assumed to be 284.8 eV.

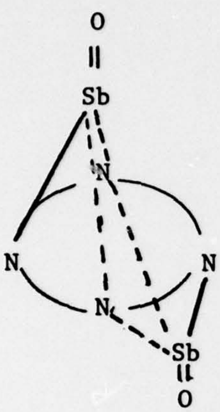
The binding energies measured for the antimony 3d spin-orbit doublet are 530.9 eV for $3d_{5/2}$ and 540.3 eV for $3d_{3/2}$. Each component of the doublet is relatively narrow and symmetrical having a full width at half-maximum height (FWHM) of approximately 1.8 eV. Similar FWHM values at Sb 3d peaks had been observed by Tricker for a series of antimony halide complexes, e.g., K_2SbF_5, $Cs_3Sb_2Br_9$ and $CsSbCl_6$ etc. [6a]. Each complex contains antimonies of having only one kind of oxidation state, III or V. Especially, K_2SbF_5 consists of crystallographically equivalent antimony atoms and of two groups of four equivalent flourines resulting in approximately square-pyramidal geometry of isolated SbF_5^{2-} [7]. In contrast, Sb $3d_{5/2}$ and $3d_{3/2}$ spectra of Cs_4Sb(III) Sb(V)Cl_{12} is considerably broader (FWHM = 3.4 eV) than the 3d region spectra of materials containing Sb(III) or Sb(V) alone [6b]. The broadening of the Sb_{3d} spectra has been attributed to contributions to the total observed spectra from both Sb(III) and Sb(V) sites. The deconvolution of the spectra gave rise to two superimposed peaks approximately 1:1 area ratio separated in energy by about 1.5 eV. The observed FWHM value of 1.8 eV for phthalocyanine complex, thus, suggests that the antimony atoms

in the complex are chemically equivalent to each other. The structure Pc:Sb•Sb:Sb•Sb:Pc which was proposed by Barrett et al. is then inappropriate to describe antimony phthalocyanine complex.

The $Sb3d_{5/2}$ and $3d_{3/2}$ binding energies observed for a series of Sb(III) complexes except fluoroantimonates(III) [8] vary from 530.1 eV to 531.0 eV and from 539.3 eV to 540.2 eV, respectively. Although we cannot simply conclude an oxidation state of a metal atom in a complex only from the binding energy data of the metal, the $Sb3d_{5/2}$ and $3d_{3/2}$ binding energies of the phthalocyanine complex seem to be in the range of trivalent antimony's values. It should be further noted that the Sb 3d region spectrum of the phthalocyanine complex accompanies a noticable oxygen 1s peak at 533.0 eV. Similar measurements of 3d region spectra for antimony(III) halide complexes did not show evidence for any oxygen 1s signal [4]. These ESCA results and elemental analysis indicate that a formula $PcSb(III)O_2$ is the most reliable for the antimony phthalocyanine complex. Another possible formula $PcSb(III)_2(OH)_4$ can be excluded by reasons that (1) elemental analysis does not fit well to the formula and (2) the IR spectrum does not show any strong OH-stretching signals around 2800 $\sim$ 3600 cm^{-1}.

As shown in Figure 2, two separate peak were recorded in the N_{1s} spectrum of antimony phthalocyanine complex at 398.7 eV and 400.2 eV with FWHM of 1.4 eV. This is marked contrast with N_{1s} spectra of the other metal-phthalocyanine complexes where only one sharp signal is observed. The profile of the single sharp peak has been attributed to a small energy separation between four equivalent central nitrogens and four meso-bridging nitrogens. In these complexes a metal binds equivalently with the central four nitrogens. Antimony phthalocyanine ($PcSb(III)_2O_2$), however, is not the case and its N_{1s} spectrum is even similar to the pattern of the spectrum of metal-free phthalocyanine H_2Pc. The most reliable explanation for the data is that there are two kinds of central nitrogen in the complex which are presumably those with and without antimonies attached [9]. The

ESCA results being kept in mind, we propose the structure 1 or 2 for the antimony phthalocyanine complex. We do not rule out some weak interaction between antimony and central nitrogens in 1 or 2 which do not combine directly with antimony.



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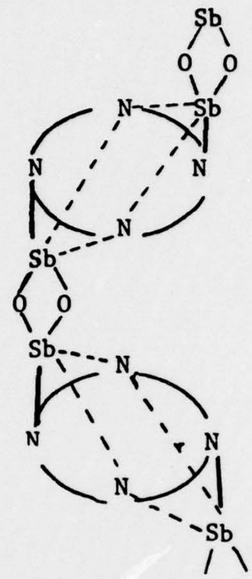

2.

The resonance Raman data observed for $PcSb(III)_2O_2$ and H_2Pc are summarized in Table 1. As Table 1 shows, the patterns of these spectra are very similar to each other except the region 250 ∿ 450 cm^{-1}. The similarity of the Raman spectra accords well with that of N_{1s} photoelectron spectra between $PcSb(III)_2O_2$ and H_2Pc. The peaks characteristic of antimony phthalocyanine in the range of 250 ∿ 450 cm^{-1} may be attributable to Sb=O, Sb-N and/or Sb-O vibration modes.

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8. Fluroantimonates(III) gives slightly higher binding energies for Sb_{3d} peaks; for $3d_{5/2}$, 531.2 $\sim$ 531.5 eV and for $3d_{3/2}$, 540.5 $\sim$ 540.8 eV.

9. The observed intensity ratio of the two N_{1s} peaks ($\sim$ 2/1) was lower than the expected ratio (3/1). Usually the ratio is reduced by possible satellite peaks at higher energy regions than each of main peaks and by surface contamination.

TABLE 1. Observed Raman frequencies (cm^{-1}) for antimony phthalocyanine complex and metal-free phthalocyanine.

ANTIMONY PHTHALOCYANINE

207 (w)	228 (m)	297 (w)	313 (w)	345 (w)
449 (w)	480 (w)	538 (w)	564 (m)	677 (s)
719 (m)	792 (s)	1004 (w)	1020 (w)	1062 (w)
1078 (m)	1100 (m)	≃1114 (sh)	1136 (m)	1178 (w)
≃1205 (sh)	≃1227 (w)	≃1310 (sh)	1333 (s)	1363 (w)
≃1385 (sh)	1403 (m)	1422 (m)	1445 (m)	1468 (m)
1507 (s)	1523 (s)	≃1536 (sh)	1579 (vw)	1609 (m)

METAL-FREE PHTHALOCYANINE

206 (w)	227 (m)	479 (w)	536 (w)	562 (m)
677 (s)	718 (m)	791 (s)	1001 (w)	1021 (w)
1062 (vw)	1077 (m)	1099 (m)	≃1110 (sh)	1135 (m)
1177 (w)	1198 (vw)	1222 (w)	1286 (vw)	≃1308 (w)
1332 (s)	≃1360 (vw)	1384 (w)	1400 (m)	1420 (m)
1443 (m)	1506 (s)	1523 (s)	1535 (sh)	1578 (vw)
1608 (m)				

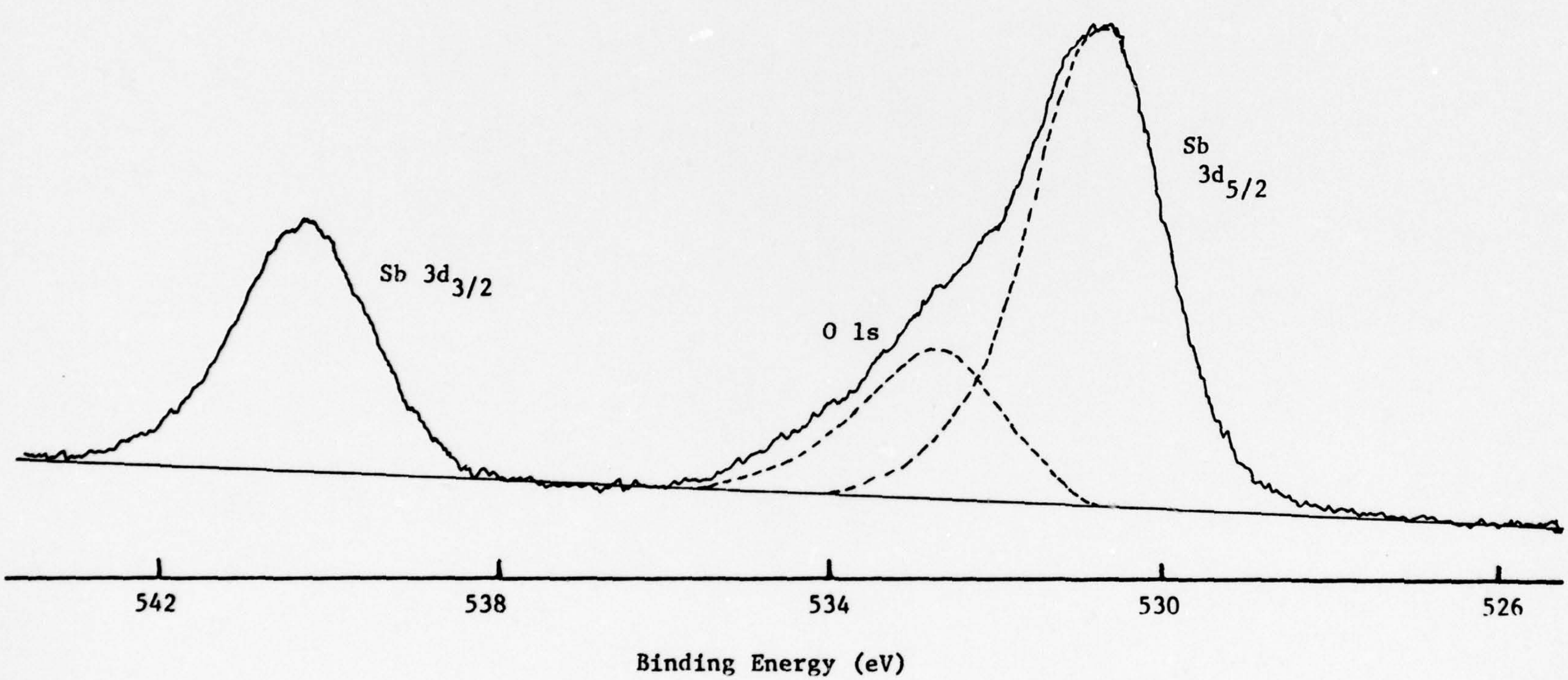
* Values underlined are peaks characteristic of antimony phthalocyanine.

s = sharp, m = medium, w = weak, vw = very weak, sh = shoulder

FIGURE CAPTIONS

Figure 1. Sb_{3d} region photoeclectron spectrum of antimony phthalocyanine. O_{1s} peak is accompanied in the spectrum.

Figure 2. N_{1s} photoelectron spectrum of antimony phthalocyanine. Deconvolution of the two components is given by the dotted line.


Sb 3d3/2
O 1s
Sb
3d5/2
542
538
534
530
526
Binding Energy (eV)